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EVALUATION OF REGENERATIVE FUEL CELL

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1. INTRODUCTION

The majority of the effort in the past three months has been expended on the design and construction of equipment which will permit a high quality development program to be pursued. A considerable amount of time has been expended in developing the best cell for developmental tests. Though this has held up actual experimental development work, the extra effort expended in developing a good cell has already borne fruit.

Two accomplishments have been achieved:

1. Previous tests had indicated that stainless steel No. 304 was inert enough (possibly due to an impervious coating of MnO_2) to permit its use as a cell container material without it entering into the electrochemical reaction. Thorough development work should eliminate this possibility altogether, though, and therefore it was decided to design nylon and teflon cells. It was thereby discovered when cells made of teflon containers were used, that the power density of the cell was increased by a factor of two, by doubling of the discharge voltage and retention of the high charge-discharge voltage efficiency (61⁰/o).
2. The teflon cells have met the discharge requirement of 35 minutes. Cells were discharged at 1.1 volts for 35 minutes. The voltage stayed constant at 1.1 volts after the first two minutes of discharge (see Figure 6). It appears that this performance

cannot be duplicated in the stainless steel cells (though this is not definite yet).

The remainder of this report is divided into two sections discussing (1) the design and construction of equipment on the program, and (2) the experiments already performed, as well as those being planned under an intensive effort in the next two months.

2. DESIGN AND CONSTRUCTION OF EQUIPMENT

2.1 Test Cell Models

Seven designs for test cell models have been tried. Five main problems were to be solved by these designs. The cells should have:

- a. Non-corrosive cell containers.
- b. Seals which do not leak at high internal pressures.
- c. Preferably an electrically highly resistant cell container.
- d. A design permitting easy assembly and disassembly.
- e. A compact internal volume without recesses or small volumes leading off from the main volume.

Four of the designs coming closest to meeting these specifications are discussed below.

Cell design No. 1, shown schematically in Figure 1, is of stainless steel construction with stainless-clad thermocouples soldered through the walls to make the electrical contact with the electrodes. The alumina insulation in the thermocouple leads is protected from attack by the KOH with epoxy resin. The cell is sealed by means of a teflon O-ring.

The main drawbacks of this cell are the fact that the thermocouple wires are fragile and must be replaced after each

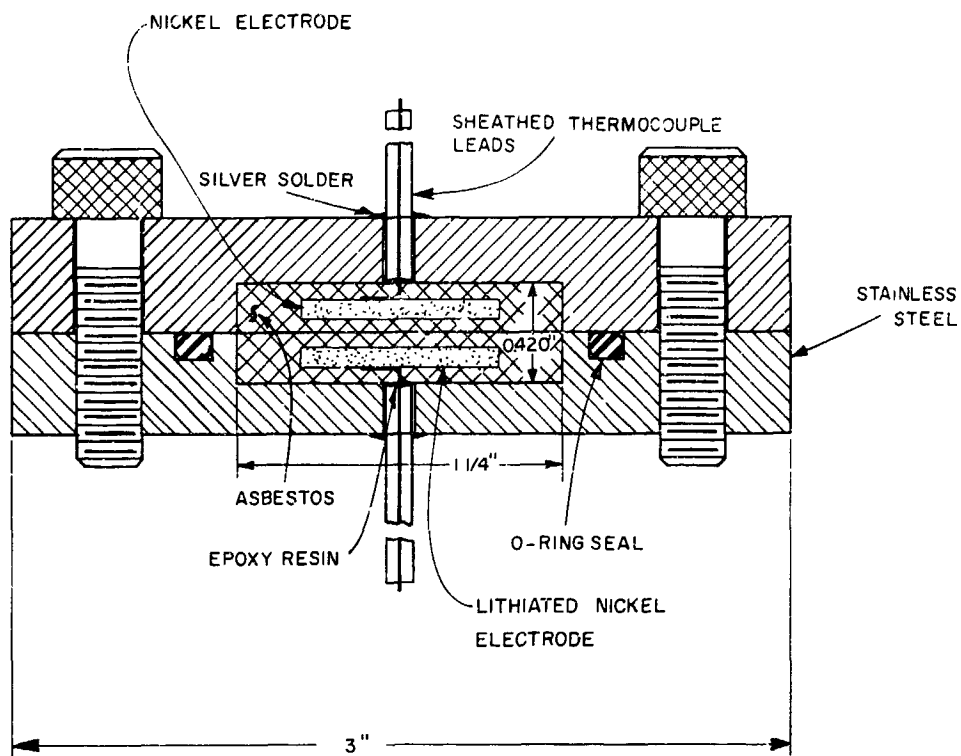


FIG. 1 FUEL CELL NO. 1

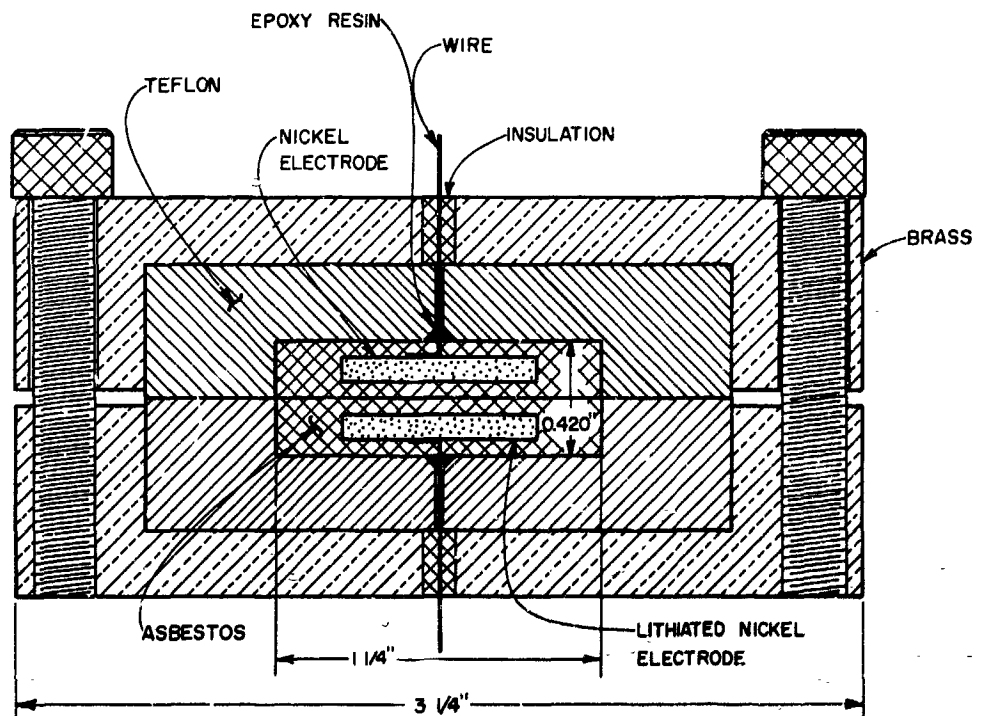


FIG. 2 FUEL CELL NO. 2

one or two runs. This is time consuming and inconvenient.

Furthermore, the presence of the stainless cell appears to have a deleterious effect on cell performance as explained below.

Cell design No. 2, the teflon cell, shown schematically in Figure 2, suffers from the fact that the epoxy resin sealing the wire through the teflon must be replaced after each run.

Cell design No. 3, shown schematically in Figure 3, does not require sealing of electrical leads through the walls of the cell, but does present a large stainless area for possible undesirable electrochemical reaction. An advantage of this design is the ease of machining. It is planned to teflon coat this cell so that no stainless surface will be accessible to the electrolyte. Nickel electrode contact strips will penetrate the teflon coating to provide electrical contact.

Cell design No. 4, shown schematically in Figure 4, employs a nylon cell body, a teflon O-ring seal, and compressed teflon lead-through seals for the nickel contact wires. This cell has none of the disadvantages of the above three cells; however, the nylon is slowly attacked by the KOH at 155°C.

Therefore, modifications of designs No. 3 or No. 4 with teflon coated metal parts, or the use of nickel parts coated with green nickel oxide (which has high electrical resistance and corrosion resistance as explained in British Patent No. 725,661) is planned.

2.2 Pressure Transducer

It is very important to follow the pressure changes within the cell, in relation to the state of charge or discharge in order to learn enough about the cell reaction to allow intelligent cell designing.

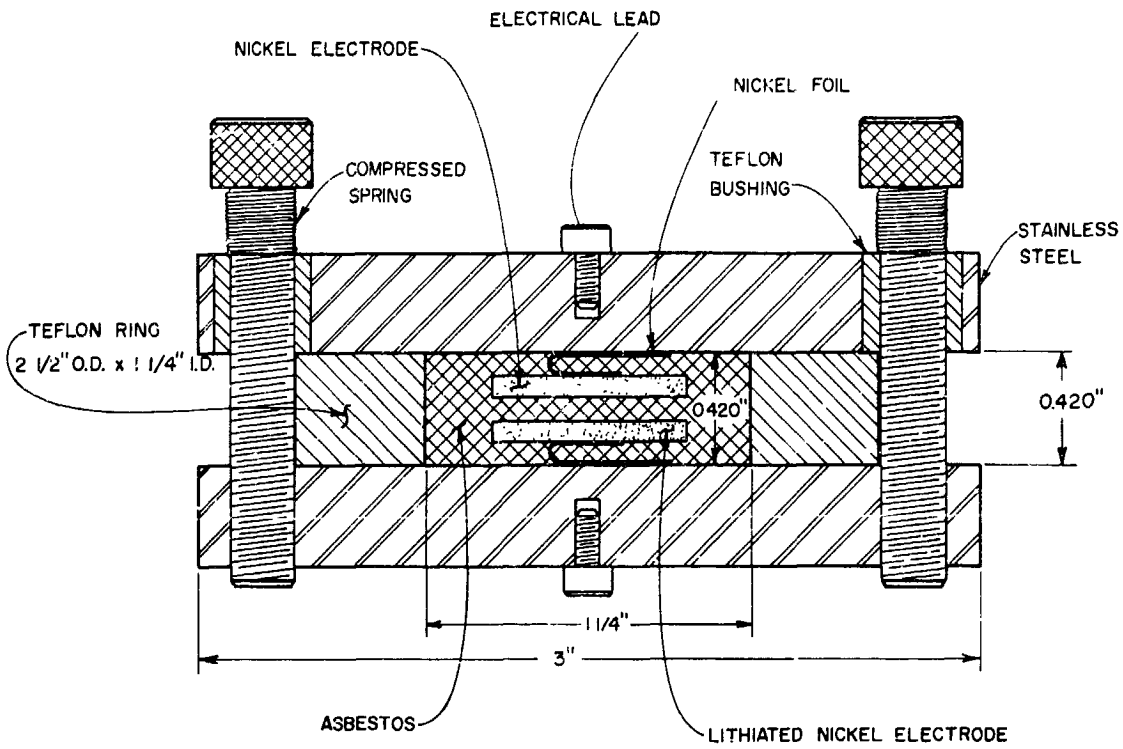


FIG. 3 FUEL CELL NO. 3

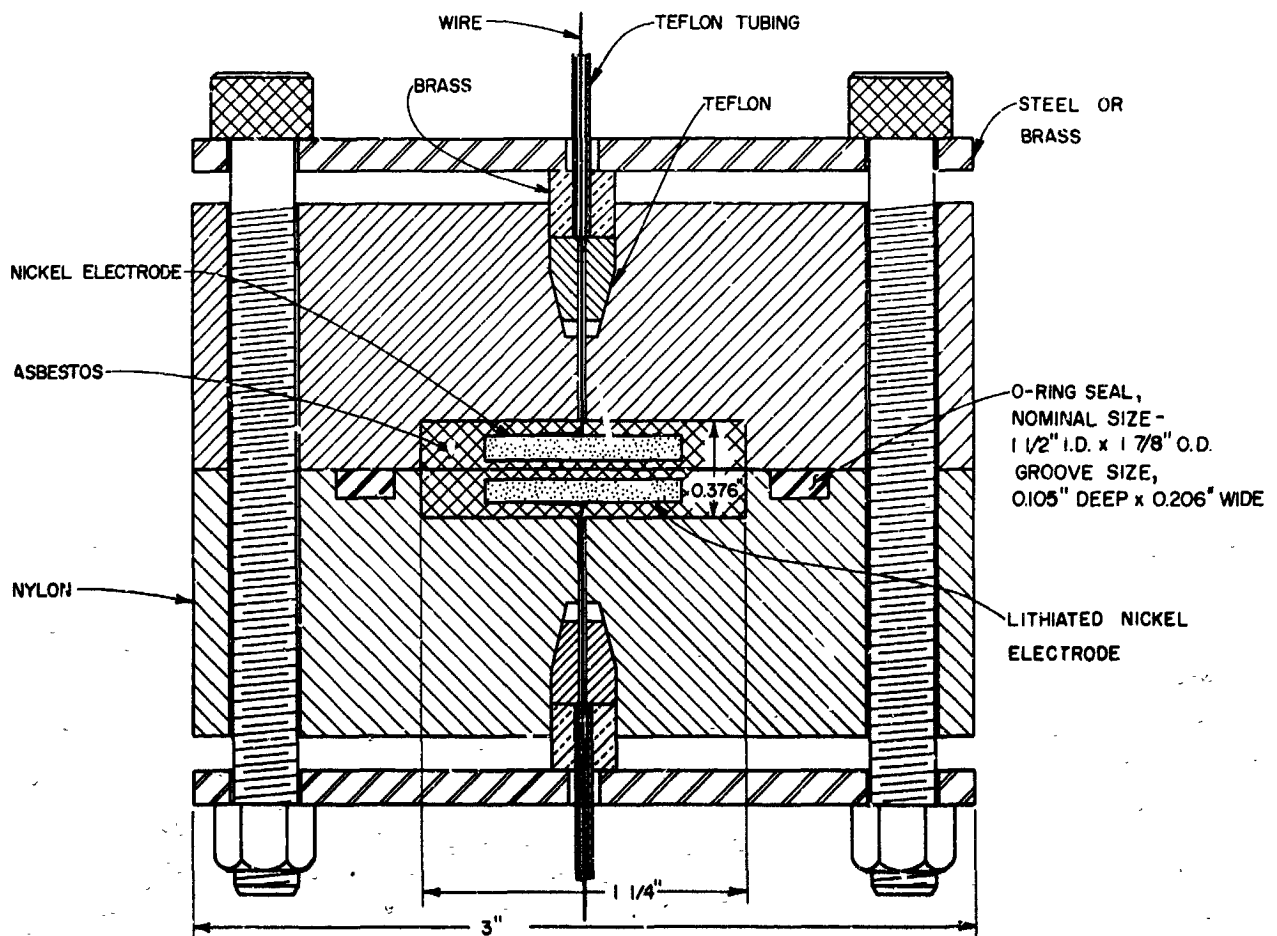


FIG. 4 FUEL CELL NO. 4

This pressure determination will be possible by mounting a flush diaphragm pressure transducer so that it is flush with the wall of the cell. A strain gauge transducer was incorporated in a cell but it could not adequately be protected from corrosion by the electrolyte solution.

Pace Engineering Company of North Hollywood, California has built their Model P25 variable reluctance pressure transducer out of nickel instead of the usual stainless material. The unit has one integral surface, instead of having several parts held together by soldered seams. For these reasons the unit should resist corrosion. It has a 0-300 psi range and can be used to 350°F. It is used in conjunction with the Pace CD-10 carrier modulator.

2.3 Manual Test Equipment

Dual facilities were set up to permit two independent experiments to be run concurrently. Control panels were made to permit complete control of the charging and discharging rates (variation either in steps or continuous) of fuel cell models, while simultaneously permitting continuous monitoring of voltage and current. The measurements can be made either on multirange voltmeters and ammeters mounted in the panels, or on automatic recorders attached to suitable plug-in outlets. All switching of leads between charge and discharge cycles, as well as open circuit settings can be obtained virtually instantaneously by manipulating one switch.

The cells are heated in small drying ovens controlled with bimetallic regulators. The actual temperature of the cells are recorded on strip chart recorders or observed with indicating thermocouple pyrometers.

Two recorders are in use on the experiments, for voltage and current recording.

1. Brush Recorder Mark II

2. Brown "Elektronik" - 24 channel,

2 second print speed, 1 - 240 inches/hour
using INSCO chart speed changers.

2.4 Automatic Cycling Equipment

The system consists of the following circuits, as shown in Figure 5:

1. Charging circuit for the fuel cell
2. Protection circuit for an excess charging voltage of the fuel cell
3. Discharging circuit for the fuel cell
4. Protection circuit for the fuel cell so as not to be discharged lower than a certain voltage.

The automatic switching circuit consists of an actuator 3 p.d.t. operated by a cam. The total period for charge and discharge of the fuel cell is one hundred minutes. The timing for charge/discharge ratio could be adjusted to any combination between 10°/o - 90°/o, or 90°/o - 10°/o of the cycling period. The charging voltage is twenty volts and is regulated to better than .5°/o from no load to full load. The charging current and the discharging current can be set between 100 microamperes to 1.1 ampere. The percentage of variation for the charging or discharging current is:

$$\frac{+ \Delta V_{F.C.}}{20 V + V_{F.C.}} \times 100$$

$\Delta V_{F.C.}$ = voltage variation of the fuel cell either during charge or discharge period

$V_{F.C.}$ = the voltage of the fuel cell at the beginning of the charging or discharging cycle

Provision has been made for the Brown recorder mentioned in 2.3 above to record the voltage of the fuel cell during the cycling period.

Protection circuitry is in process of development. It will be set manually to automatically open the circuit when the voltage of the fuel cell reaches a certain voltage.

3. EXPERIMENTAL PROGRAM

Not much discussion will be given of experimental results to date. Until more experiments can be performed using the new equipment which has been set up, no conclusions can be drawn.

3.1 Results to Date

Figure 6 shows that after a four minute charge at 600 ma, it was possible to obtain 34 minutes discharge at 21 ma. Cell No. 2 was used. The electrodes were 7/8" diameter. The effect of changing the internal geometry and size of the cell, changing the charge and discharge rates and times, etc., is not yet known. It is anticipated that the program outlined below will greatly increase the amp-hour efficiency of the data in Figure 6.

3.2 Program Anticipated for January and February

Both manual and automatic equipment will be used.

3.2.1 Manual Equipment

The following data will be obtained (with pressure being recorded by the transducer) on modified versions of cells No. 3 or No. 4.

- a. E - I Curves
- b. E and I vs. time of charge and discharge up to 100 min. per cycle
- c. Retention of charge as a function of time
- d. a, b, c, above as a function of temperature
- e. a and b above with variation of the following parameters
 1. Amount of lithiation of the O₂ electrode

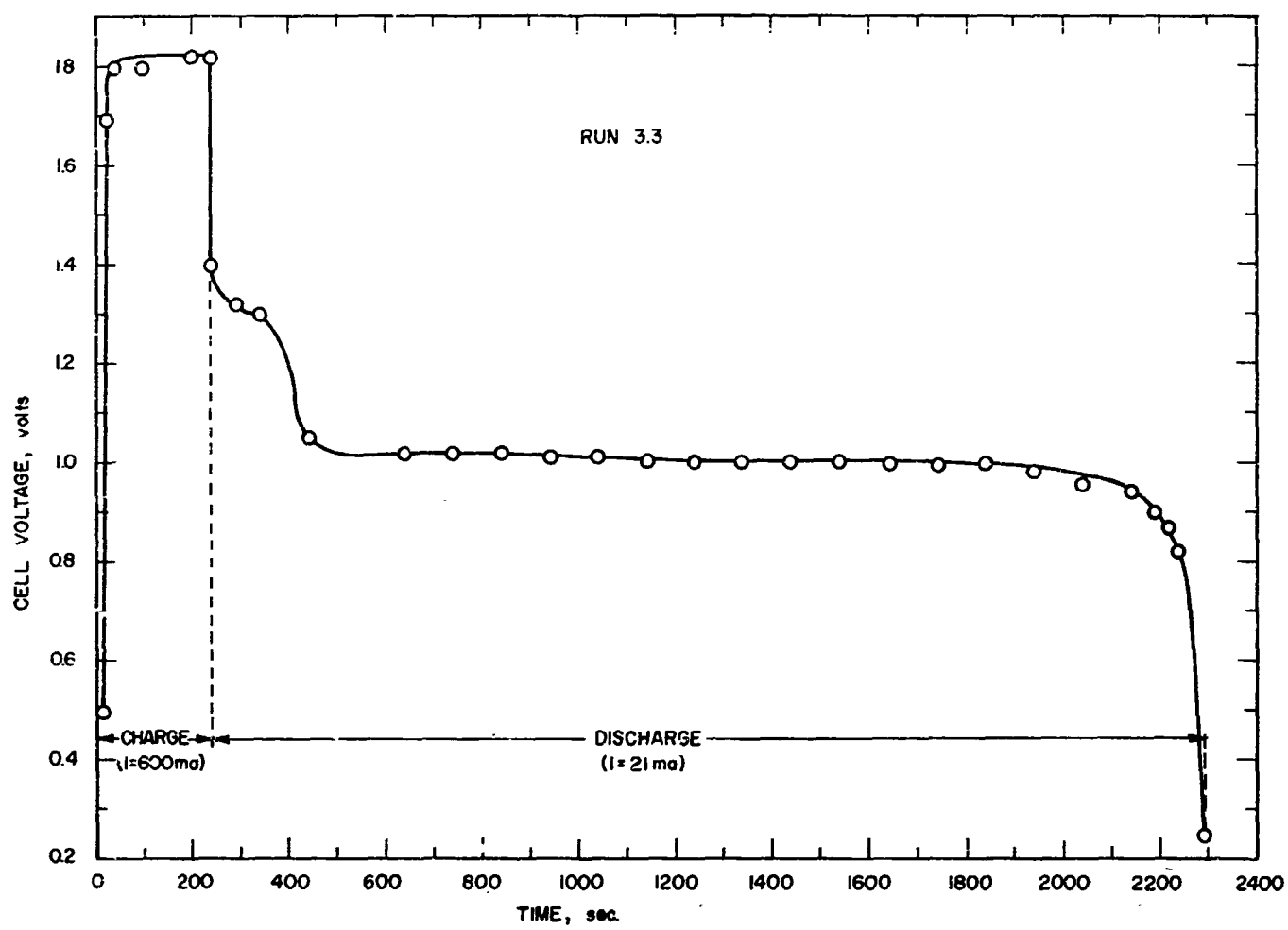


FIG. 6 CHARGE-DISCHARGE CURVE (FUEL CELL NO. 2)

2. Amount of asbestos
3. Replacement of asbestos by porous MgO, or Al₂O₃ (only if time permits)
4. KOH amount and concentration
5. Variation of electrode and asbestos porosities (perhaps, if time permits)
6. Asbestos/void space ratio and variation of internal geometry of cell
7. Catalyzed carbon instead of lithiated nickel O₂ electrode
8. H₂ - Br₂ cell replacing H₂ - O₂ cell to evaluate advantage of Br₂ electrode
9. Use of AgO as O₂ storage material. Also other O₂ solid storage material is to be tried

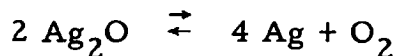
3.2.2 Automatic Cycling Equipment

Superior cell models will be placed on automatic cycling and voltage at constant current will be recorded for many 160 minute cycles.

3.2.3 Additional Comments

Some thought has been given to the possibility of reducing the gas pressure in the fuel cell by reaction of the oxygen with a suitable metal or metal oxide to form, respectively, the oxide or peroxide.

The silver-silver oxide equilibrium is of particular interest:



Using the data of G. N. Lewis¹, as shown in Table I, a van't Hoff plot gives the dissociation pressure at 150°C (302°F) of 266 mm.

TABLE I

Dissociation Pressure of Argentous Oxide

<u>t (°C)</u>	<u>P (atm)</u>
302	20.5
325	32.0
445	207.0

Hence, provided that the kinetics are favorable, silver oxide in equilibrium with silver should keep the partial pressure of oxygen sufficiently low so as to obviate the necessity for a high pressure cell while simultaneously permitting the pressure to be sufficiently high so as to permit the cell to operate at reasonable power density. Also, the use of the silver would decrease any thermal reaction of H_2 and O_2 which might occur over the longer cycle times.

The silver electrode would then become a "silver oxide" or "silver peroxide electrode" rather than an "oxygen gas" electrode. It would behave similarly to silver electrodes in conventional storage batteries. The possibility of using a carbon electrode between the silver powder and the hydrogen electrode would force the actual formation of O_2 gas, and would permit the use of an intermediate inert electrode. Whether this is desirable or not will have to be ascertained by experiments. The use and preparation of catalyzed carbon O_2 electrodes is well known².

Since bromine is much more reversible than oxygen as an oxidizing agent in aqueous solution, it would be worthwhile to try the cell as a $H_2 - Br_2$ cell with a $NaBr - HBr$ electrolyte.

REFERENCES


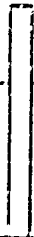

1. G. N. Lewis, Z. Physical Chemistry, 55, 449 (1906)
2. H. Hunger, "Investigation of the H_2-O_2 Fuel Cell; "
ASTIA - AD 219732 (1958)

4. MAN-HOURS EXPENDED

2,239 man hours total have been expended on this contract
as of 17 December 1960.

5. PROGRAM SCHEDULE

	Dec.	Jan.	Feb.	March
I. Experiments with Manual Equipment				
a) E - I curves				
b) E and I vs. time of discharge up to 65 min.				
c) Retention of charge as a function of time				
d) a, b, c, above as a function of temperature				
e) a and b above with variation of the following parameters				
1) Amount of lithiation of the O ₂ electrode				
2) Amount of asbestos				
3) KOH amount and concentration				
4) Asbestos/void space ratio and variation of internal geometry of cell				
5) Catalyzed carbon instead of lithiated nickel O ₂ electrode				
6) H ₂ -Br ₂ cell replacing H ₂ -O ₂ cell to evaluate advantage of Br ₂ electrode				
7) Use of AgO as O ₂ storage material. Also other O ₂ solid storage material is to be tried				

	Dec.	Jan.	Feb.	March
II. Design and Construction of Cell Optimized for 35-65 minute cycle				
III. Placement of Cells on Automatic Cycling				
IV. Preparation of Final Report				